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(54) PHOTOELECTRIC CONVERSION ELEMENT AND MANUFACTURING METHOD THEREFPR

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a photoelectric conversion element which carries large amount of sensitizing coloring matters and has superior photoelectric conversion characteristics.

SOLUTION: In a photoelectric conversion element at least comprising an electrode, where the layer of metal oxide semiconductor is attached to one side of the electrode, a pair electrode which faces the layer of metal oxide semiconductor of the electrode, and a layer of electrolyte which is placed between the layer of a metal oxide semiconductor of the former electrode and the pair electrode, causing sensitizing coloring matters to be carried on the surface of each of metal oxide semiconductor powders, which constitute the layer of metal oxide semiconductor.

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CLAIMS

[Claim(s)]

[Claim 1] The optoelectric transducer characterized by sensitizing dye being supported by the front face of each metal oxide semiconductor particle which constitutes said metal oxide semiconductor layer in the optoelectric transducer which has the electrolyte layer arranged at least between the electrode with which the metal oxide semiconductor layer was put on one field, the counter-electrode which stands face to face against said metal oxide semiconductor layer of this electrode, and said metal oxide semiconductor layer and counter-electrode of this electrode.

[Claim 2] The electrode with which the sensitizing dye support metal oxide semiconductor layer was put on one field at least, In the manufacture approach of an optoelectric transducer of having the electrolyte layer arranged between the counter-electrode which stands face to face against said metal oxide semiconductor layer of this electrode, and said metal oxide semiconductor layer and counter-electrode of this electrode Said sensitizing dye support metal oxide semiconductor layer the substrate which has said electrode A metal halogenide complex, The manufacture approach of the optoelectric transducer characterized by being formed by making it dry after being immersed into the

water solution which has sensitizing dye and the scavenger of halogenide ion and taking out.

[Claim 3] It is the approach according to claim 2 which said metal halogenide complex is a titanium fluorocomplex, and is characterized by the scavenger of said halogenide ion being a boric acid or aluminum.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the optoelectric transducer which consists of an oxide semiconductor, and its manufacture approach. Furthermore, this invention relates to the optoelectric transducer which consists of an oxide semiconductor containing sensitizing dye, and its manufacture approach at a detail.

[0002]

[Description of the Prior Art] The solar battery is greatly expected as a clean energy source, and the pn junction mold solar battery etc. is already put in practical use. On the other hand, although the photogalvanic cell which takes out

electrical energy using the chemical reaction of an optical-pumping condition was developed by many researchers, when saying about utilization, the high pn junction mold solar battery of a track record was not already attained to far.

[0003] The type which used the oxidation reduction reaction which consists of a sensitizer and an electron acceptor in the conventional photogalvanic cell is known. For example, there is a system which combined thionine dye and iron (II) ion. Moreover, the photogalvanic cell using the photocharge separation of a metal or its oxide has also been known since discovery of the Honda-Fujishima effectiveness. When a semi-conductor contacts a metal, the Schottky barrier is made due to the work function of a metal and a semi-conductor, but same junction can be performed also when the semi-conductor and the solution have touched. For example, when oxidation reduction systems, such as Br^- [Fe^{2+}/Fe^{3+}, $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$, I^- / I_2, and]/Br_2, and hydroquinone/quinone, are included in the solution, if a n-type semiconductor is attached to a solution, the electron near the front face of a semi-conductor will move to the oxidizer in a solution, and will reach equilibrium. Consequently, near the front face of a semi-conductor is just charged, and an electric potential gradient produces it. In connection with this, inclination arises also in the conduction band and valence band of a semi-conductor.

[0004] If light is irradiated on the front face of the semiconductor electrode

attached to the oxidation reduction solution, light with the energy more than the band gap of a semi-conductor is absorbed, and near a front face, an electron will be generated to a conduction band and it will generate an electron hole to a valence band. The electron excited by the conduction band is transmitted to the interior of a semi-conductor according to the electric potential gradient which exists near the front face of the semi-conductor mentioned above, and, on the other hand, the electron hole generated by the valence band takes an electron from the reductant in a oxidation reduction solution. If a metal electrode is dipped in a oxidation reduction solution and a circuit is made between a metal electrode and a semi-conductor, the reductant from which the electron was taken in the electron hole will diffuse the inside of a solution, will receive an electron from a metal electrode, and will be returned again. this cycle -- repeating -- a semiconductor electrode -- in a metal electrode, each can supply power to ****** and the exterior as a positive electrode as a negative electrode. Therefore, photoelectromotive force becomes the difference of the oxidation reduction level of a oxidation reduction solution, and the Fermi level in a semi-conductor. In order to enlarge photoelectromotive force, it is being able to make a big difference, namely, using the large semi-conductor of a band gap between using the strong oxidation reduction solution of oxidizing power low [1 oxidation-reduction level], 2 oxidation-reduction level, and the Fermi level in a

semi-conductor.

[0005] However, if the oxidizing power of a oxidation reduction solution is too large not much, an oxide film is formed in the own front face of a semi-conductor, and a photocurrent is stopped in the inside of a short time. Moreover, generally about a band gap, there is a problem which a band gap tends to dissolve into a solution according to the current on which 3.0eV or less semi-conductor 2.0 moreeV or less flows in the case of photo electric conversion. For example, by underwater optical exposure, n-Si forms an inactive oxide coat in a front face, and dissolves n-GaAs and n-CdS in it in oxidation. The device which covers a protective coat is tried by the semi-conductor in these problems at the ****** sake, and the device which uses p mold conductive polymers, such as polypyrrole which has electron hole transport properties, and the poly aniline, the poly thiophene, for the protective coat of a semi-conductor is proposed. However, a problem is in endurance and it was stabilized only about several days at most. Although a band gap can consider 3eV or more of use of a certain semi-conductor in order to solve the problem of the optical dissolution, a strong peak is too large for absorbing the sunlight near 2.5eV efficiently. Therefore, only an ultraviolet region can be absorbed among sunlight, and the visible region which occupies most is not absorbed at all, but conversion efficiency becomes very low.

[0006] In order to reconcile a deployment of a light region, and the light stability of the big semi-conductor of a band gap, the coloring matter sensitization solar battery which made the semi-conductor support the sensitizing dye which absorbs the light by the side of long wavelength smaller than the band gap of a semi-conductor is known. A different place from the wet solar battery using the conventional semi-conductor is a photocharge separation process which light is irradiated at coloring matter, an electron is excited, and an excitation electron moves to a semi-conductor from coloring matter.

[0007] A coloring matter sensitization solar battery is related with photosynthesis, and is caught in many cases. Although chlorophyll was considered like photosynthesis as coloring matter at the beginning, it was what unlike the natural chlorophyll exchanged for continuously new chlorophyll there is a problem in respect of stability, and does not fill the conversion efficiency as a solar battery with the coloring matter used for a solar battery to 0.5%, either. It is very difficult to simulate the process of photosynthesis of a nature as it is, and to constitute a solar battery.

[0008] Thus, although a coloring matter sensitization solar battery obtains a hint from photosynthesis and it is said that it would absorb the light of long wavelength, since the electronic conduction device became complicated in fact, increase of loss became a problem. If the layer which absorbs light is thickened,

absorption efficiency can be raised in a solid solar battery. However, about a coloring matter sensitization solar battery, only the monomolecular layer on a front face can pour an electron into a semiconductor electrode. Therefore, in order to lose the useless absorption of light, as for the coloring matter on a semi-conductor front face, considering as a monomolecular layer is desirable. And in order to pour in the electron in the excited coloring matter into a semi-conductor efficiently, it is desirable to have combined with the semi-conductor front face and the chemistry target. For example, in order to combine with a semi-conductor front face and a chemistry target about titanium oxide, it is important that a carboxyl group is in coloring matter etc. Fujihira's and others group did the important improvement about this point. They have reported to Magazine Nature that the photocurrent became 10 or more times of the conventional adsorption process in 1977, when the carboxyl group of rhodamine B carries out an ester bond to the hydroxyl group of SnO2 front face. This is made because the pi orbital in which the electron with which the direction of an ester bond absorbed luminous energy within coloring matter exists is nearer than the conventional amide association on the surface of a semi-conductor. However, the electron which is in a conduction band even if it is able to pour an electron into a semi-conductor effectively has possibility of recombining with the ground level of coloring matter, possibility of recombining with the oxidation

reduction matter, etc. Since there was such a trouble, conversion efficiency was still low in spite of the above-mentioned improvement about electron injection.

[0009] As mentioned above, it is that only the sensitizing dye supported with the monolayer by the semi-conductor front face can pour in an electron to a semi-conductor as a big trouble of the conventional coloring matter sensitization solar battery. That is, the single crystal and polycrystal semi-conductor which were used well [until now] to a semiconductor electrode have a smooth front face, the effective area with which it does not have pore in the interior but sensitizing dye is supported is equal to an electrode surface product, and there are few amounts of support of sensitizing dye. Therefore, when such an electrode is used, the sensitizing dye of the monomolecular layer supported by the electrode can be absorbed 1% or less of incident light also on the maximum absorption wavelength, but the use effectiveness of light gets very bad. Although the attempt which makes sensitizing dye a multilayer is also proposed in order to heighten the light-harvesting force, sufficient effectiveness is not acquired generally. As a means to solve such a problem, GURETTSUERU etc. porosity-ized the titanium oxide electrode and increased remarkably the internal area which makes sensitizing dye support (for example, the patent No. 2664196 official report). This titanium oxide porous membrane is produced with a sol-gel method, membranous porosity is about about 50%, and the nano porosity

structure of having very high specific surface area is formed. For example, in 8-micrometer thickness, a roughness factor (real area inside the porosity over substrate area comparatively) amounts also to about 720. When this front face is calculated geometrically, the concentration of sensitizing dye will give 1.2xten - seven mols /to 2 cm, and about 98% of incident light will be absorbed very much on the maximum absorption wavelength.

[0010] The new coloring matter sensitization solar battery called this GURETTSUERU cel is the description that the point which absorbed efficiently increase of the fast amount of support of the sensitizing dye by porosity-izing of above-mentioned titanium oxide and sunlight, and sensitizing dye with it developed is big. [the remarkable electron injection rate to a semi-conductor and] [quick]

[0011] GURETTSUERU and others developed the bis(bipyridyl) (II) Ru complex for the coloring matter sensitization solar battery. The Ru complex has the structure of the general formula cis--X2 screw (2, the 2'-bipyridyl -4, 4'-dicarboxy rate) (II) Ru. X is Cl-, CN-, and SCN-. Fluorescence, light absorption, and electrochemical and research systematic about photooxidation reduction-behavior were done about these. among these -- cis--(diisocyanate)-having the engine performance which boiled markedly Screw (2, the 2'-bipyridyl -4, 4'-dicarboxy rate) (II) Ru as a solar light absorption agent and a coloring

matter sensitizer, and was excellent was shown.

[0012] Light absorption of this coloring matter sensitizer is charge transfer transition to a ligand from a metal. Moreover, the carboxyl group of a ligand is directly configurated to surface Ti ion, and forms close electronic contact between a coloring matter sensitizer and titanium oxide. It is supposed that re-capture of the electron poured in to the conduction band of the titanium oxide by the coloring matter sensitizer to which the electron injection from a coloring matter sensitizer to the conduction band of titanium oxide happened at the very quick rate of one or less picosecond, and that hard flow oxidized by this electronic contact is happened to the order of a microsecond. This speed difference produces the directivity of an optical-pumping electron, and charge separation is the reason performed at very high effectiveness. And it is the difference from the pn junction solar battery which performs charge separation according to the electric potential gradient of a pn junction side, and this is prodigal and is the essential description of a TSUERU cel.

[0013] The configuration of a GURETTSUERU cel is the cel of the sandwiches mold which enclosed the electrolytic solution containing a redox couple between two conductive glass substrates which coated the transparence electric conduction film of the tin oxide which carried out the fluorine dope. One side of a glass substrate carries out the laminating of the porous membrane which

consists of titanium oxide ultrafine particles of colloid on the transparence electric conduction film, makes sensitizing dye adsorb further and is taken as a working electrode. Another side coats a small amount of platinum on the transparence electric conduction film, and makes it a counter electrode. A spacer is inserted between two glass substrates and an electrolytic solution is poured into very few clearances between in the meantime using capillarity. The mixed solvent of ethylene carbonate and an acetonitrile is used for an electrolytic solution, and it is what made the solute iodation tetra--n-propyl ammonium and iodine, and contains the redox couple of I-/I3-. The platinum by which coating was carried out to the counter electrode has the catalysis which carries out cathodic reduction of I3- of this redox couple to I-.

[0014] The principle of operation of a GURETTSUERU cel is not different from the wet solar battery which used the conventional semi-conductor fundamentally. However, in every part of a porous electrode like a GURETTSUERU cel, the photocharge separation response of homogeneity and being carried out efficiently is mainly because the hole moving bed is a liquid. That is, it is because a solution diffuses in porosity in homogeneity only by dipping a coloring matter support porous electrode in a solution and an ideal electrochemical interface can be formed. However, even if this hole moving bed actually produces [as for a solution layer] a cell preferably from a viewpoint of the stability of a solar battery

in many cases, the liquid spill of an electrolytic solution precedes with degradation of other cell components, and happens, and reducing the engine performance of a solar battery is known. For utilization of a GURETTSUERU cel, as the electrolyte was mentioned as an example, an examination detailed about each element which constitutes a GURETTSUERU cel must be added.

[0015] as mentioned above, it is the description of a GURETTSUERU cel boiling a roughness factor markedly, having raised it using the ultrafine particle of titanium oxide, and having enlarged the amount of sensitizing dye support. Consequently, photoelectric conversion efficiency higher than the conventional coloring matter sensitization solar battery is realized. Therefore, in order to acquire higher photoelectric conversion efficiency, it becomes a technical problem how the amount of support of sensitizing dye is increased.

[0016] As a solution of this technical problem, adding high density to an oxide semiconductor, and adding water for sensitizing dye to a hydrophilic organic solvent, in order to make it support firmly is indicated by JP,10-290021,A.

[0017] Furthermore, the heating reflux art is indicated by JP,7-249790,A.

[0018] Drawing 3 is the flow chart showing the production process of the conventional coloring matter sensitization solar battery. First, oxide semiconductors, such as titanium oxide, are applied to transparence substrates, such as glass, in step 301. Subsequently, in step 302, an oxide semiconductor is

calcinated at the temperature of about 500 degrees C. Then, a baking oxide semiconductor is made to support sensitizing dye in step 303. Subsequently, the electrolytic solution is applied to this glass substrate in step 304. After applying the electrolytic solution, in step 305, a glass substrate is closed and a coloring matter sensitization solar battery is prepared.

[0019] Drawing 4 is the outline sectional view of the structure obtained in step 303 of the conventional approach as shown in drawing 3 . It applies to the front face of the transparent electrode 3 formed on one front face of the transparence glass substrate 1, and sensitizing dye 7 is supported by the calcinated oxide-semiconductor particle layer 5 as illustrated. By heating the oxide-semiconductor particle applied to the glass substrate at about 500 degrees C, a part of oxide-semiconductor particles sinter, and the porosity oxide-semiconductor particle layer 5 is formed. The part which can support sensitizing dye with the conventional sensitizing dye support approach of making an oxide-semiconductor particle layer immersed in a sensitizing dye solution, within an oxide-semiconductor particle layer is only a field which has a bigger opening than sensitizing dye. Therefore, when sensitizing dye cannot be supported into an opening part smaller than sensitizing dye but a coloring matter sensitization solar battery is prepared, the field will become the part inactive in photochemistry with which only the electrolytic solution was merely filled. For this

reason, in the conventional coloring matter sensitization solar battery, the amount of the sensitizing dye supported by the oxide-semiconductor particle will become restrictive, and the photoelectric transfer characteristic of a solar battery will not be improved so much as a result, either.

[0020]

[The technical problem which invention tends to settle] Therefore, the purpose of this invention is offering the optoelectric transducer which supports a lot of sensitizing dye and has the outstanding photoelectric transfer characteristic.

[0021]

[Means for Solving the Problem] Said technical problem is [after adding the scavenger (for example, a boric acid or aluminum) of halogenide ion in the water solution containing the metal halogenide complex (for example, titanium fluorocomplex) which is a precursor of an oxide semiconductor, and sensitizing dye] solvable by immersing a substrate in the solution by forming in a substrate front face the oxide semiconductor film which supported a lot of sensitizing dye.

[0022]

[Embodiment of the Invention] Since the manufacture approach of the oxide semiconductor which supported sensitizing dye by this invention makes an oxide semiconductor support sensitizing dye, making the precursor of an oxide semiconductor react, sensitizing dye can combine with an oxide semiconductor

strongly, and it can make the amount of support abundant and high density. By increasing the amount of support of sensitizing dye, the photoelectric conversion efficiency of an optoelectric transducer increases by leaps and bounds. Furthermore, according to this invention, the sensitizing dye support oxide-semiconductor film suitable for an optoelectric transducer can be formed at 1 time of the process of making a substrate immersed in the reaction mixture of a room temperature.

[0023] Drawing 1 is the flow chart showing the manufacture approach of the optoelectric transducer by this invention. In step 101, the coloring matter support titanium oxide film by the liquid phase depositing method is produced as illustrated. The liquid phase depositing method is explained to a detail below. Then, in step 102, the electrolytic solution is applied and, subsequently a substrate is closed in step 103. Electrolytic-solution spreading of step 102 and the closure of step 103 are generally the same as electrolytic-solution spreading of the conventional approach and closure processing which were shown in drawing 3 .

[0024] Drawing 2 is the schematic diagram of the coloring matter support oxide-semiconductor film formed by the liquid phase depositing method of this invention. The oxide-semiconductor particle 11 has deposited on the front face of the transparent electrode 3 formed on one front face of the transparence glass

substrate 1. According to this invention, sensitizing dye 9 is supported by the outside surface of each oxide-semiconductor particle 11. Thereby, the sensitizing dye support oxide-semiconductor film 13 is formed.

[0025] Although sensitizing dye 9 is supported by the outside surface of the oxide-semiconductor particle 11, it is thought with it being actual that it is supported by both the interior of an oxide-semiconductor particle and the exterior. Although the exact mechanism with which sensitizing dye is supported by the oxide-semiconductor particle is not yet solved, it is thought that it is supported when various factors, such as chemical association, physical association, and electrostatic adsorption or physicochemical adsorption, act independently complexly and in collaboration. Thus, according to the liquid phase depositing method of this invention, since each oxide-semiconductor particle can be made to support sensitizing dye, the amount of support of sensitizing dye can be increased by leaps and bounds. Therefore, like the conventional approach, as a result of being unable to support sensitizing dye to an opening smaller than sensitizing dye, it is lost that a field inactive in photochemistry will be made and the outstanding photoelectric conversion efficiency can be acquired.

[0026] The vocabulary the "liquid phase depositing method" used in this specification means how to make a generation metallic oxide support sensitizing

dye at the same time it makes a metallic oxide generate in the liquid phase. The liquid phase depositing method by this invention consists of a (1) metallic-oxide formation reaction and two staircase reactions of (2) coloring-matter support reaction.

[0027] (1) A metallic-oxide formation reaction is shown by the following reaction formula.

TiF62-+H2O -> TiO2 ** +6F-+4 H+BO3-+4F-+6H+-> BF4-+3H2O[0028] (2) A coloring matter support reaction is shown by the following reaction formula.

TiO2** + RuL2(NCS)2 -> TiO2-RuL2(NCS)2[0029] All of these reactions are performed in the same water solution. For example, if the scavenger and sensitizing dye of a metal halogenide complex and halogen ion are dissolved in water and a water solution is prepared, the above (1) and the reaction of (2) can advance serially in this water solution, and sensitizing dye support oxide-semiconductor film like TiO2-RuL2(NCS) 2 can be made to form on the surface of a substrate by immersing a substrate into this water solution.

[0030] Although 10 degrees C - 80 degrees C of this reaction of (1) and (2) can generally be preferably carried out in the temperature ambient atmosphere within the limits of 20 degrees C - 60 degrees C, it is desirable to carry out at the temperature a room temperature or near ordinary temperature. Generally under such temperature conditions, a reaction is performed over the period for 1 hour -

five days. Generally, if reaction temperature is high, reaction time will become short, and reaction time will become long if reaction temperature is low. As an example, with the reaction temperature of 30 degrees C, a reaction is started within about 15 - 30 minutes, and the oxide-semiconductor film can be produced on a substrate by the almost fixed rate of sedimentation till about 80 hours. As for a substrate, it is desirable that you make it immersed with a posture perpendicular in a reaction water solution or suitable before a reaction is started. Although a substrate can also be immersed after a reaction is started, the generated coloring matter support oxide semiconductor condenses, and the film with a big particle size may be formed. (1) At the reaction of a formula, as for the boric acid which is the scavenger of halogen ion, concentration decreases as a reaction advances. Then, if the monitor of the boric-acid concentration is carried out with a pH stat plan so that boric-acid concentration may become fixed during a reaction, the homogeneous coloring matter support oxide-semiconductor film can be formed. Moreover, when using aluminum as a scavenger, equivalent effectiveness can be acquired by supplying aluminum to a reaction solution with a fixed time interval.

[0031] Since the amount of support of about [that thickness distribution becomes homogeneity] and coloring matter will increase if the coloring matter support oxide-semiconductor film is made to form in a substrate front face under

a free convection ambient atmosphere, it is desirable to make the coloring matter support oxide-semiconductor film form in a substrate front face under a free convection ambient atmosphere. Although a reaction water solution can also be stirred in order to promote a reaction, the oxide-semiconductor particle which precipitates in a reaction process distributes in a reaction solution, it is incorporated by the coloring matter support oxide-semiconductor film deposited on a substrate, and there is a possibility that thickness distribution may become an ununiformity. Then, while filtration removes precipitate, the device of circulating a reaction solution in the fixed rate of flow is required.

[0032] It is desirable to remove the reaction mixture which picked out the substrate from the reaction water solution after reaction termination, washed the substrate front face with the suitable solvent for washing, and remains in the front face. As a solvent for washing, alcohols, such as a methanol besides water, such as purified water, distilled water, pure water, and ultrapure water, or ethanol, can also be used, for example. Other solvents can also be used.

[0033] It is desirable to make this substrate season naturally after washing a substrate front face with the solvent for washing. If a forced drying is carried out, since a crack etc. will occur on the coloring matter support oxide-semiconductor film formed in the substrate front face, it is not desirable. Therefore, desiccation is about 10-40-degree C a room temperature or ordinary temperature, and it is

desirable to carry out in the ambient atmosphere of 80% - about 40% of relative humidity. Moreover, about humidity, at the desiccation initiation time, it is high humidity of 80% of relative humidity, and it is desirable to spend the period of about 1 hour and to make it fall to about 40% of relative humidity gradually, attaining thermal equilibrium after that. By carrying out like this, quality sensitizing dye support oxide-semiconductor film which is not, such as a pinhole, and a crack or a cracking crack, can be obtained.

[0034] In this invention, as a metal halogenide complex, although both a metaled fluoride a chloride a bromide and an iodide complex can be used, it is desirable, balance to the fluoride, i.e., the metal fluorocomplex, of a hydrolysis rate, and the adsorption and the desorption rate to a substrate. Especially as a metal fluorocomplex, it is not limited and the fluorocomplex of the element which constitutes fluorocomplexes, such as fluorocomplexes, such as titanium, a zirconium, a hafnium, vanadium, niobium, a tantalum, chromium, molybdenum, and a tungsten, iron, nickel, zinc, silicon, and tin, or perovskite etc. is mentioned. Or it is also possible to combine these fluorocomplexes.

[0035] As an oxide semiconductor used for an optoelectric transducer, the oxide of Cd, Zn, In, Pb, Mo, W, Sb, Bi, Cu, Hg, Ti, Ag, Mn, Fe, V, Sn, Zr, Sr, Ga, Si, and Cr, perovskite like SrTiO3 and CaTiO3, etc. are desirable. Since the electron by which optical pumping was carried out with Ru complex is efficiently

poured into titanium oxide when Ru complex is used as sensitizing dye, the coloring matter sensitization solar battery which consists of an Ru complex and titanium oxide has the outstanding property. Therefore, a titanium fluorocomplex is desirable especially as a precursor of the oxide semiconductor which constitutes an optoelectric transducer. As for the titanium fluorocomplex which can be used by this invention, for example, a hexafluoro titanic acid, hexafluoro titanic-acid (IV)2 lithium, hexafluoro titanic-acid (IV) disodium, hexafluoro titanic-acid (IV)2 potassium, hexafluoro titanic-acid (IV) magnesium, hexafluoro titanic-acid (IV) calcium and hexafluoro titanic-acid (IV) barium, hexafluoro titanic-acid (IV)2 ammonium, etc. are mentioned. However, other titanium fluorocomplexes can also be equally used by this invention.

[0036] As a scavenger of the halogenide ion which separates in a reaction water solution by advance of a reaction, especially if advance of the hydrolysis reaction of the aforementioned metal halogenide complex is not barred, it will not be limited. Especially as a scavenger which can fulfill such conditions, a boric acid and aluminum are desirable.

[0037] In this invention, the concentration of the scavenger of a metal halogenide complex and halogenide ion will not be especially limited, if the target oxide semiconductor can be prepared. For example, titanium oxide can be prepared, if the concentration of a titanium fluorocomplex is a 0.15 mols [/l.] density range

from 0.01 mols/l. and the concentration of a boric acid is 0.1 mols/l. or more, when preparing titanium oxide using a titanium fluorocomplex and a boric acid. It is desirable to prepare titanium oxide especially with the reaction solution whose concentration of a boric acid the concentration of a titanium fluorocomplex is 0.1 mols/l., and is 0.2 mols/l. The above-mentioned concentration is an example, and if the ratio of concentration of a titanium fluorocomplex and a boric acid is selected according to the concentration of these above, it cannot be overemphasized that titanium oxide can be prepared. When producing the oxide-semiconductor film used for an optoelectric transducer with this reaction solution, 60-degree-C [20 degrees C to] range of reaction temperature is desirable.

[0038] All can be used if it is coloring matter of daily use by the conventional coloring matter sensitization nature optoelectric transducer as sensitizing dye in this invention. Such coloring matter is well-known to this contractor. Such sensitizing dye is a phthalocyanine or a porphyrin of a transition metal complex the ruthenium-cis--JIAKUA-bipyridyl complex of for example, RuL2(H2O) 2 type or ruthenium-tris (RuL3), a ruthenium-screw (RuL2), male NIUMU-tris (OsL3), and male NIUMU-bis(OsL2) type, a metal, or a nonmetal etc. As an example, for example, a cis--JI (thio cyano)-N and N-bis(2, 2'-bipyridyl -4, 4'-dicarboxy rate) ruthenium (II) complex, Ruthenium-tris (2, 2'-screw pyridyl -4, 4'-dicarboxy rate),

A ruthenium-cis--JIAKUA-screw (2, 2'-screw pyridyl -4, 4'-dicarboxy rate), a zinc-tetrapod (4-carboxyphenyl) porphyrin, an iron-hexa cyanide complex, a phthalocyanine, etc. are mentioned. As organic coloring matter, 9-phenyl xanthene dye, coumarin system coloring matter, an acridine dye, triphenylmethane dye, tetraphenylmethane system coloring matter, quinone system coloring matter, azo dye, indigo system coloring matter, cyanine dye, merocyanine system coloring matter, a xanthene dye, etc. are mentioned.

[0039] The amount of the sensitizing dye used can be drawn from the aforementioned reaction formula to stoichiometric. For example, sensitizing dye can be used by the metallic oxide generated at the metallic-oxide formation reaction of the above (1), the equimolecular amount, or more molar quantity than this. In order to acquire sufficient photoelectric-transfer-characteristic improvement effect, it is desirable to use a lot of sensitizing dye than the molar quantity of the metallic oxide generated. According to this invention, the metal oxide semiconductor film can be made to support two or more 50 ng/cm sensitizing dye at least.

[0040] If it sees from a viewpoint of the optimal model, sensitizing dye will occupy space in the state of the close-packed structure, and the condition that titanium oxide exists in the opening will be considered to be the condition of having made titanium oxide carrying out the maximum support of the sensitizing

dye by the liquid phase depositing method. If this amount of support is estimated, since the magnitude of Ru complex is about 3nm, molecular weight is 741 and the voidage in the maximum dense condition is 25.9%, the amount of the maximum support of Ru complex will be set per three and to 1/(4/3xpix3 (3x10-7))x(1-0.259)x(741 / 6.02x1023) =8.06mg 1cm, for example. On the other hand, since the consistencies of titanium oxide are 3.9 g/cm3 in an anatase mold and titanium oxide exists only in the opening in the maximum dense condition, the consistency of titanium oxide serves as 3.9x0.259=1.01 g/cm3. Therefore, the amount of the maximum support of Ru complex by the liquid phase depositing method can be estimated at 7.98mg per 1g of titanium oxide.

[0041] The optoelectric transducer by this invention consists of an electrode which has the sensitizing dye support oxide-semiconductor film produced by the liquid phase depositing method of this invention, and the counter electrode and the electrolyte enclosed among them. As an electrode to which the sensitizing dye support oxide-semiconductor film is made to adhere, transparent conductive glass, a transparent conductive polymer sheet, etc. are mentioned. Since membranes can be formed, especially the optoelectric-transducer manufacture approach of this invention can use a transparent conductive flexible substrate without heating baking processing as an electrode. Since the conventional approach was accompanied by the heating baking processing by high

temperature like 500 degrees C, as a substrate, only heat-resistant substrates, such as glass, could be used and flexible substrates, such as plastics with heat-resistant low temperature, were not able to be used. By using flexible substrates, such as plastics, as a substrate, the application of optoelectric transducers, such as a solar battery as a final product, is expanded. What carried out the coat of the platinum to transparent conductive glass, a transparent conductive polymer sheet, etc. as a counter electrode is desirable.

[0042] Although it will not be especially limited if the oxidation reduction system constituent of a pair which consists of an oxidant and a reductant is contained in the solvent as an electrolyte, the oxidation reduction system constituent in which an oxidant and a reductant have the same charge is desirable. The oxidation reduction system constituent in this specification means the matter of the pair which exists in the form of an oxidant and a reductant reversibly in an oxidation reduction reaction. The oxidation reduction system constituent itself [such] is well-known to this contractor. The oxidation reduction system constituent which can be used by this invention For example, chlorine compound-chlorine, Iodine compound-iodine, a bromine compound-bromine, thallium ion (III)-thallium ion (I), Mercury ion (II)-mercury (ion I) ruthenium ion (III)-ruthenium ion (II), Copper ion (II)-copper ion (I) iron ion (III)-iron ion (II), Vanadium ion (III) / - vanadium ion (II) manganic acid ion-permanganic acid ion, ferricyanide-ferrocyanide, a

quinone-hydroquinone, a fumaric-acid-succinic acid, etc. are mentioned. Needless to say, other oxidation reduction system constituents can also be used.

[0043] A solvent is used, in order to dissolve the electrolyte which consists of an oxidation reduction system constituent and to prepare the electrolytic solution. Although both an aquosity solvent and an organic solvent can be used as a solvent, since an oxidation reduction system constituent is stabilized more, an organic solvent is desirable. For example, dimethyl carbonate, diethyl carbonate, methylethyl carbonate, methyl propionate, ethylene carbonate, propylene carbonate, butylene carbonate, a gamma butyrolactone, an ethylene glycol ape fight, 1, 2-dimethoxyethane, 1, 3-dioxo silane, a tetrahydrofuran, a 2-MECHIRU tetra-hydra furan, diethylether, etc. are mentioned. These can also be used independently, respectively, and can also mix and use two or more kinds together. Furthermore, an amine system, an imide system or a nitril system solvent, a ** sulfur system or a fluorine-containing organic solvent, etc. can be used. In this invention, the mixed solvent of ethylene carbonate and an acetonitrile is desirable.

[0044]

[Example] Hereafter, an example illustrates this invention concretely.

[0045] Production hexafluoro titanic-acid (IV)2 ammonium 0.1mol/l. of the example 1(1) sensitizing-dye support oxide semiconductor film, In the water

solution in which cis--JI (thio cyano)-N and N-bis(2, 2'-bipyridyl -4, 4'-dicarboxy rate) ruthenium (II) complex 0.3 millimol / I was dissolved as a 0.2 mols [/l.] boric acid and sensitizing dye The glass substrate with a transparent electrode (50mm x 50mm) was made immersed perpendicularly, and it was made to react at 30 degrees C for 20 hours. In order to make only a transparent electrode deposit the titanium oxide which supported sensitizing dye, the mask of the glass side except a transparent electrode was carried out. This electrode was washed in order of ultrapure water and ethanol, and was made to season naturally after reaction termination. The thickness of the titanium oxide which supported the sensitizing dye deposited on the transparent electrode was 300nm.

[0046] (2) As a counter electrode of a glass substrate with a transparent electrode which has the titanium oxide film which supported the production sensitizing dye of an optoelectric transducer, the glass substrate with a transparent electrode (50mm x 50mm) which carried out the spatter of the platinum was prepared. As the electrolytic solution, the electrolytic solution made to dissolve 0.04 mols [/l.] iodine, iodation tetrapropylammonium 0.5mol/l. in the mixed solution of the volume ratio 8:2 of ethylene carbonate and an acetonitrile was prepared. After it inserted the separator with a thickness of 100 micrometers as the mutual electrode side faced these two electrodes each other, and pouring the above-mentioned electrolytic solution into inter-electrode by capillarity, the

perimeter was closed, the terminal was pulled out from each electrode, and the optoelectric transducer of this invention was produced.

[0047] It is the following, and the content of the sensitizing dye in the sensitizing dye support titanium oxide film produced above (1) was made and measured. The sensitizing dye support titanium oxide film produced above (1) was immersed in the ethanol solution of 0.1 mols/l. of sodium hydroxides which is the measuring method which first is already known well, and elution of the Ru complex which is sensitizing dye was carried out. However, by this measuring method, elution only of some supported Ru complexes could not be carried out, and Ru complex remained into the titanium oxide film. Since Ru complex in the titanium oxide film cannot pass through an opening smaller than itself, this is considered were not able to be eluted from the titanium oxide film. That is, this phenomenon is considered to be expression of the effectiveness that the liquid phase depositing method can make many sensitizing dye support from a conventional method. Then, as reference of Ru complex support titanium oxide film, the thin film of only titanium oxide was produced by the same approach as the above (1), and both absorption spectrums were measured. The amount of support of Ru complex was calculated from absorbance change of Ru complex support titanium oxide film in the absorption wavelength of Ru complex. Moreover, the xenon lamp light of 45 mW/cm2 was irradiated at the optoelectric

transducer produced above (2) (exposure area 12cm2), and the photocurrent-voltage characteristics, such as an open end electrical potential difference, a short-circuit current consistency, a form factor, and photoelectric conversion efficiency, were measured by the I-V curve tracer.

[0048] The glass substrate with a transparent electrode (50mm x 50mm) was made perpendicularly immersed in the water solution in which example of comparison 1 hexafluoro titanic-acid (IV)2 ammonium 0.1mol/l., and a 0.2 mols [/l.] boric acid were dissolved, and it was made to react to it at 30 degrees C for 20 hours. Then, this glass substrate was calcinated at 500 degrees C, and the titanium oxide film was formed. Then, the ethanol solution of cis--JI (thio cyano)-N and N-bis(2, 2'-bipyridyl -4, 4'-dicarboxy rate) ruthenium (II) complex 0.3 millimol / l was made immersed as sensitizing dye for 3 hours, and the titanium oxide film was made to support sensitizing dye. A glass substrate is picked out from a sensitizing dye ethanol solution, and it washed in order of ultrapure water and ethanol, and was made to season naturally. As a counter electrode of a glass substrate with a transparent electrode which has the obtained sensitizing dye support titanium oxide film, the glass substrate with a transparent electrode (50mm x 50mm) which carried out the spatter of the platinum was prepared. As the electrolytic solution, the electrolytic solution made to dissolve 0.04 mols [/l.] iodine, iodation tetrapropylammonium 0.5mol/l. in the

mixed solution of the volume ratio 8:2 of ethylene carbonate and an acetonitrile was prepared. After it inserted the separator with a thickness of 100 micrometers as the mutual electrode side faced these two electrodes each other, and pouring the above-mentioned electrolytic solution into inter-electrode by capillarity, the perimeter was closed, the terminal was pulled out from each electrode, and the optoelectric transducer for comparison contrast was produced. Subsequently, the sensitizing dye content and the photocurrent-voltage characteristic in the titanium oxide film were measured by the same approach as said example 1.

[0049] The photoelectric transfer characteristic and the sensitizing dye content of an optoelectric transducer which were obtained in said example 1 and the example 1 of a comparison are shown in the following table 1.

[0050]

[Table 1]

Open end electrical potential difference Short-circuit current consistency Form factor Photoelectric conversion efficiency The amount of sensitizing dye (V) (mA/cm2) (%) (ng/cm2) Example 1 0.80 0.49 0.22 0.19 Example 1 of 200 comparisons 0.73 0.02 0.46 0.01 30 [0051] Since sensitizing dye is supported by the titanium oxide particle of each [optoelectric transducer / which has the sensitizing dye support oxide semiconductor film of this invention] itself so that clearly from the result shown in Table 1, compared with the conventional

optoelectric transducer, a sensitizing dye content increases by about 7 times, consequently photoelectric conversion efficiency increases also 19 times.

[0052] Added 0.7g of aluminum complications in 250ml of water solutions in which example 2 hexafluoro titanic-acid (IV)2 ammonium 0.1mol/l., and the ruthenium complex 0.3 millimol / l same as sensitizing dye as an example 1 were dissolved, the glass substrate with a transparent electrode (50mm x 50mm) was made perpendicularly immersed in them, and it was made to react to them at 30 degrees C for 16 hours. In order to make only a transparent electrode deposit the titanium oxide which supported sensitizing dye, the mask of the glass side except a transparent electrode was carried out. This electrode was washed in order of ultrapure water and ethanol, and was made to season naturally after reaction termination. The thickness of the titanium oxide which supported the sensitizing dye deposited on the transparent electrode was 280nm. As a result of SEM observation, the same surface type voice as an example 1 was shown, and it checked that both a boric acid and aluminum could be used as a scavenger of fluoride ion.

[0053]

[Effect of the Invention] Since an oxide semiconductor is made to support sensitizing dye according to this invention as explained above, making the precursor of an oxide semiconductor react, sensitizing dye can combine with an

oxide semiconductor strongly, and can make the amount of support abundant and high density. By increasing the amount of support of sensitizing dye, the photoelectric conversion efficiency of an optoelectric transducer increases by leaps and bounds. Furthermore, according to this invention, the sensitizing dye support oxide-semiconductor film suitable for an optoelectric transducer can be formed at 1 time of the process of making a substrate immersed in the reaction mixture of a room temperature.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] Drawing 1 is the flow chart by the liquid phase depositing method of this invention showing the production process of an optoelectric transducer.

[Drawing 2] Drawing 2 is the schematic diagram of the coloring matter support oxide-semiconductor film formed by the liquid phase depositing method of this invention.

[Drawing 3] Drawing 3 is the flow chart showing the production process of the conventional optoelectric transducer.

[Drawing 4] Drawing 4 is the outline sectional view of the structure obtained in

step 303 of the conventional approach as shown in drawing 3 .

[Description of Notations]

1 Glass Substrate

3 Transparent Electrode

5 Oxide-Semiconductor Layer

7 Sensitizing Dye Layer

9 Sensitizing Dye

11 Oxide-Semiconductor Particle

13 Sensitizing Dye Support Oxide-Semiconductor Film